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(54) Photosensitive materials comprising organic photoconductive substances in a binder polymer having aromatic rings, OH groups and bromine joined at the aromatic ring or rings.

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**Description**

This invention relates to photosensitive materials for electrophotography which make use of organic photoconductive compounds or substances dispersed in a specific type of binder polymer and which are particularly suitable for use in electrophotographic systems using a charging/exposing/developing process.

As is known in the art, photosensitive compounds or substances which have been used in the field of electrophotography are broadly classified into inorganic photoconductors and organic photoconductors. Typical examples of the inorganic photoconductor include selenium, zinc oxide, titanium oxide, cadmium sulfide and the like. Typical examples of the organic photoconductors include phthalocyanine pigments and diazo pigments.

The photosensitive material using the inorganic photoconductor is not always satisfactory with respect to the thermal stability and the durability. With inorganic photoconductors which are, in most case, toxic, there are problems on their preparation and handling.

On the other hand, a photosensitive material using the organic photoconductor is free of any toxic problem with excellent productivity and good economy. In addition, organic photoconductors can be arbitrarily controlled in photosensitive characteristic by modification or proper designing of the molecule. Accordingly, developments of organic photoconductors have been extensively made and organic photoconductors are now being predominantly employed in the field of electrophotography.

Known organic photosensitive materials have usually a double-layer structure which includes a carrier generation layer capable of absorbing light to generate carriers and a carrier transport layer wherein the generated carriers are transported. Many attempts have been made for higher sensitivity. For attaining high sensitivity in the double-layer structure, the usual practice is that the carrier generation layer is formed in a thickness of several micrometers and the carrier transport layer is formed in a thickness of several tens micrometers. In order to impart high strength and good printing resistance, it is general that the carrier generation layer is formed directly on a substrate and the carrier transport layer is formed as a surface layer. The carrier generating agent used is one which works through movement of positive holes and the resulting photosensitive material is eventually of the negative charge type.

The negative charge systems, however, have several drawbacks: (1) negative charges attack oxygen in air to produce ozone which is not only harmful to human body, but also shortens the life of the photosensitive material by reaction therewith; (2) charging does not proceed satisfactorily; (3) the system is apt to be influenced by surface properties of a substrate such as a drum.

In order to overcome the above drawbacks, organic photosensitive materials of the positive charge type have been extensively studied. In order to realize the positive charge system, attempts have been heretofore made including

(1) reversed double-layer structures wherein the carrier generation layer and the carrier transport layer are reversed to the case of the negative charge system type; and

(2) single-layer structures wherein various types of carrier generation compounds and carrier transport compounds are both dispersed in a binder resin.

However, the reversed double-layer structure involves the problems such as a lowering of the printing resistance and a poor life characteristic owing to the fact that the carrier generation layer, which has to be substantially thin, is placed on the surface of the photosensitive material. In addition, there arise problems such as complication in the fabrication process of the double-layer structure and of layer separation. Accordingly, this type of photosensitive material has not been reduced to practice yet.

The photosensitive materials having the single-layer structure are inferior to the double-layer structure photosensitive materials with respect to the sensitivity, a charging characteristic (i.e. a charging potential gradually drops when the material is repeatedly employed), and a residual potential. Nevertheless, the single-layer structure is advantageous in that if a carrier generation agent and a carrier transport agent are uniformly dispersed throughout the layer, the printing resistance is not lowered immediately after wear of the photosensitive material. This is considered for the reason that the wear of the photosensitive material does not directly influence the photosensitive characteristic. The single-layer structure is easier in fabrication than the double-layer structure. In short, the single-layer structure and the double-layer structure have, respectively, merits and demerits.

We proposed in EP-A-408380 (published after the priority dates of the present application) photosensitive materials which comprise an X-type phthalocyanine and/or  $\tau$ -type phthalocyanine dispersed in polymer binders such as polyesters, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polycarbonates, polyvinyl butyral and polyvinyl acetoacetal. This photosensitive material is convenient for use in the positive charge systems. Further studies revealed that the photosensitive material was not necessarily satisfactory with respect to the life or durability. In fact, when the material is subjected to a repetition cycle test where it is repeatedly used over 10,000 or more printing cycles, the charge voltage, attenuation in the dark and sensitivity are grad-

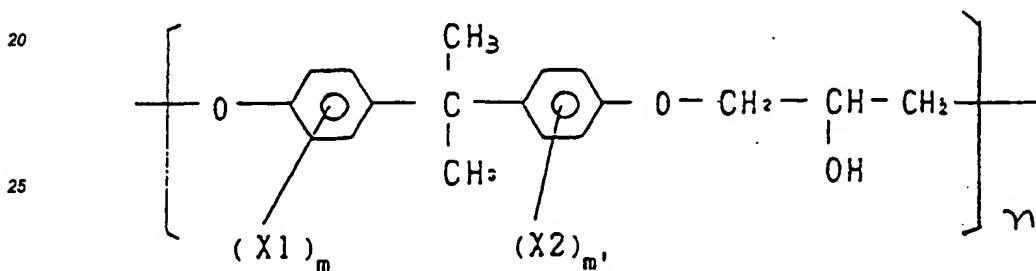
ually lowered. The reason for this is considered to result from chemical fatigue such as with light and/or ozone generated in the system

5 EP-A-104088 and FR-A-1447277 disclose photosensitive materials comprising a layer of a photoconductor dispersed in, as resin binder, a poly(hydroxyether) which may for example be derived from tetrabromobisphenol A.

The invention provides organic photosensitive materials of either a positive or negative type which can solve the problems involved in the prior art organic photosensitive materials. These photosensitive materials can be of the positive charge type with a single-layer structure or a double-layer structure and have high sensitivity and good durability.

With the organic photosensitive materials of the invention charging voltage, attenuation in the dark and sensitivity are not significantly lowered as time passes. An organic photosensitive material of the invention having a double-layer structure is usable as either a positive charge type or a negative charge type.

15 The present invention thus provides a conductive support and a layer structure formed on the support, said layer structure being made of a dispersion of an organic photoconductor in a mixture of an aromatic carboxylic acid comprising at least one benzene, naphthalene, anthracene or phenanthrene ring and a thermally cured binder polymer which has recurring units of the general formula:



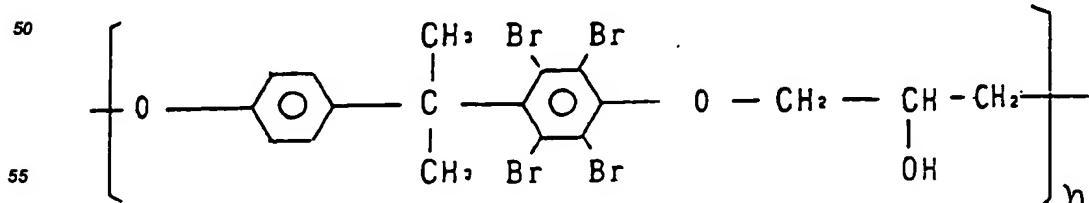
30 wherein  $X_1$  and  $X_2$  represent a bromine atom,  $m$  and  $m'$ , which may the same or different, are integers from 0 to 4, provided that  $m$  and  $m'$  are not both 0, and  $n$  is an integer of from 20 to 1000, the amount of aromatic carboxylic acid being from 2 to 30 wt % based on said binder polymer.

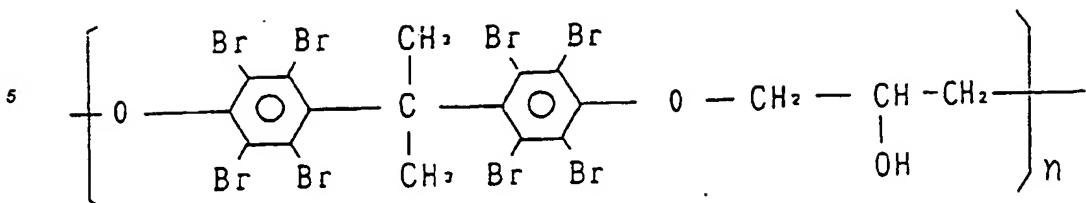
35 The layer structure may be either a single-layer structure or a double-layer structure including a carrier generation layer and a carrier transport layer. With the double-layer structure, preferably at least the surface layer should make use of the mixture of binder polymer and aromatic carboxylic acids in order to improve resistances to ozone and printing.

As described above, the photosensitive material of the invention has a layer structure on a conductive support.

40 The conductive support used in the present invention is not critical and may be made of any known materials ordinarily used for this purpose. Specific and preferable examples of the materials include metals such as aluminium, and those materials, such as glass, paper and plastics on which a conductive layer is formed such as by vacuum deposition of metals. The support may take any form such as of a drum, a belt or a sheet.

45 The layer structure formed on the conductive support is made of a dispersion of an organic photoconductor in a mixture of an aromatic carboxylic acid and a binder resin or polymer. The binder resin used has recurring units of the formula given above. For ease in preparation and chemical stability, it is preferred that four bromine atoms are joined to either or both of the benzene rings in each recurring unit. More particularly, preferable polymers have recurring units of the following formulae





These polymers are commercially available, for example, from Fuji Pharmaceutical Co., Ltd. of Japan. The photoconductors useful in the present invention may be any known ones. Examples of the photoconductors used in the invention include X-type and/or  $\tau$ -type metal-free phthalocyanine compounds treated in a specific manner and combinations of carrier generation agents and carrier transport agents. Of these, X-type phthalocyanine and/or  $\tau$ -type phthalocyanine are preferred because these phthalocyanine compounds have the capabilities of generating and transporting carriers by themselves when treated in a manner as described hereinafter. This means that when X-type phthalocyanine and/or  $\tau$ -type phthalocyanine is used, any carrier transport agent is not necessary.

15 X-type and  $\tau$ -type metal-free phthalocyanines (which may be sometimes referred to simply as H<sub>2</sub>Pc hereinafter) are described in more detail.

20 Phthalocyanine compounds include metal phthalocyanines having a metal atom at the center thereof and metal-free phthalocyanines. Typical known metal-free phthalocyanines include  $\alpha$ -type and  $\beta$ -type phthalocyanines.

25 On the other hand, X-type metal-free phthalocyanine was developed by Xerox Co., Ltd. and was reported as having excellent electrophotographic characteristics. In United States Patent No. 3,357,989, the X-type phthalocyanine is described with respect to its preparation, the relationship between the crystal form and electrophotographic characteristics and the structural analyses. According to this U.S. patent, X-type H<sub>2</sub>Pc (phthalocyanine) is prepared by subjecting  $\beta$ -type H<sub>2</sub>Pc prepared by a usual manner to treatment with sulfuric acid to obtain  $\alpha$ -type H<sub>2</sub>Pc and then to ball milling over a long time. The crystal structure of the X-type H<sub>2</sub>Pc is 30 apparently different from those of  $\alpha$ - or  $\beta$ -type H<sub>2</sub>Pc. According to the X-ray diffraction pattern of the X-type H<sub>2</sub>Pc determined by use of a CuK  $\alpha$  line, the diffraction lines appear at  $2\theta = 7.4, 9.0, 15.1, 16.5, 17.2, 20.1, 20.6, 20.7, 21.4, 22.2, 23.8, 27.2, 28.5$  and  $30.3^\circ$ . The most intense diffraction peak appears in the vicinity of  $7.5^\circ$  (corresponding to a lattice spacing,  $d = 1.18 \text{ nm} (=11.8 \text{ angstroms})$ ). When this intensity is taken as 1, the intensity of the diffraction line in the vicinity of  $9.1^\circ$  (corresponding to a lattice spacing,  $d = 0.98 \text{ nm} (=9.8 \text{ angstroms})$ ) is 1:0.66.

35 H<sub>2</sub>Pc having a crystal form other than the above form is  $\tau$ -type metal-free phthalocyanine. This phthalocyanine is obtained by subjecting to ball milling  $\alpha$ ,  $\beta$  and/or X-type crystals in an inert solvent along with a milling aid at a temperature of 5 to 10°C for 20 hours. The X-ray diffraction pattern is similar to that of X type Pc provided that the ratio of the diffraction peak intensity at about  $7.5^\circ$  and the diffraction peak intensity at about  $9.1^\circ$  is 1:0.8.

40 In the practice of the invention, the layer structure formed on the substrate may be either a single layer or a double layer.

When the X-type and/or  $\tau$ -type phthalocyanine is employed in the single layer, the phthalocyanine, the aromatic carboxylic acid and the binder resin defined before may be dispersed in a solvent system without 45 use of any charge transport agent. Preferably, the phthalocyanine, the aromatic carboxylic acid and the binder resin are mixed in a solvent system therefor until the phthalocyanine is dispersed partly in a molecular state and partly in a particulate or crystal state. By this, the X-type and/or  $\tau$ -type phthalocyanine has both capabilities of carrier generation and carrier transport. Needless to say, the starting phthalocyanine compound is 50 solid in nature at normal temperatures. More particularly, when X-type metal-free phthalocyanine and/or  $\tau$ -type metal-free phthalocyanine is mixed in a solvent therefor along with an aromatic carboxylic acid and a binder resin in such a way as set forth above and applied onto a conductive support, the resultant photoconductive layer exhibits both carrier transportability and carrier generating ability although the phthalocyanine is usually known as a carrier generating agent.

55 In a physical aspect, the exhibition of the photoconductivity is based on the X-type or  $\tau$ -type phthalocyanine which is partly dispersed in a molecular state and partly dispersed in a particulate state in the mixture of aromatic carboxylic acid and resin binder. It will be noted that the term "dispersed in a molecular state" is intended to mean the state that the X-type and/or  $\tau$ -type metal-free phthalocyanine compound is at least partially dissolved in a solvent to a satisfactory extent along with the aromatic carboxylic acid and binder resin and is dispersed in a matrix of the mixture in a molecular or dimer state after removal of the solvent and the term

"dispersed in a particulate state" is intended to mean that the original crystal form of the compound remains after dispersion in the mixture.

As stated above, part of the phthalocyanine compound should be dispersed in the mixture in a molecular state. The phthalocyanine is not readily soluble in any solvent but are at least partially soluble in a number of solvents.

In order to realize the the molecular state dispersion, the phthalocyanine compound is placed in a solvent capable of at least partially dissolving the compound therein and kneaded or mixed by means of an ordinary milling or kneading device over a long term, for example, of from several hours to several days. When the kneading operation is continued, the X-type or  $\tau$ -type phthalocyanine is finely divided and is partially dissolved. The partial dissolution is considered to be true in view of an abrupt increase of the viscosity of the mixture. It is also considered that the metal-free phthalocyanine which is in a molecular form is produced in the mixture. The molecularly dispersed metal-free phthalocyanine is assumed to have the carrier transport function.

The X-ray diffraction pattern of X-type H<sub>2</sub>-phthalocyanine after sufficient kneading or mixing along with the mixture of aromatic carboxylic acid and binder resin according to the invention apparently differs from that of X-type metal-free phthalocyanine and also differs from the X-ray diffraction patterns of  $\alpha$  and  $\beta$ -type metal-free phthalocyanines. When the X-type H<sub>2</sub>-phthalocyanine is sufficiently kneaded, the diffraction pattern has the tendency that the diffraction line over  $2\theta = 21.4^\circ$  disappears with a tendency toward an increase at about  $16.5^\circ$  as compared with the diffraction pattern of X-type H<sub>2</sub>-phthalocyanine not kneaded. The most pronounced variation is that among two diffraction peaks at about  $7.5^\circ$  ( $d = 1.18\text{mm}$  ( $=11.8\text{ angstroms}$ )) about  $9.1^\circ$  ( $d = 1.18\text{ mm}$  ( $=11.8\text{ angstroms}$ )) which are inherent to H<sub>2</sub>-Pc, only the peak at about  $7.5^\circ$  selectively disappears. This is considered as follows: the phthalocyanine crystals are converted into an amorphous state but with some possibility that an unknown crystal form may be formed from part of X-type H<sub>2</sub>-Pc.

The degree of mixing or kneading, and the mixing time and temperature depend on the type of solvent. An appropriate degree of the mixing or kneading operation can be checked by the ratio between diffraction peak intensities at about  $7.5^\circ$  and about  $9.1^\circ$  ( $I_{11.8}/I_{9.1}$ ). This ratio is preferably in the range of 1:1 to 0.1:1 for both X-type and  $\tau$ -type phthalocyanines.

The X-type phthalocyanine and/or  $\tau$ -type phthalocyanine are dispersed or dissolved in a solvent along with the mixture defined before and mixed or kneaded in, for example, a ball mill, an attritor, a sand mill or a sand grinder.

Examples of the solvent suitable for this purpose include nitrobenzene, chlorobenzene, dichlorobenzene, dichloromethane, trichloroethylene, chloronaphthalene, methylnaphthalene, benzene, toluene, xylene, tetrahydrofuran, cyclohexanone, 1,4-dioxane, N-methylpyrrolidone, carbon tetrachloride; bromobutane, ethylene glycol, sulforane, ethylene glycol monobutyl ether, acetoxyethoxyethane and pyridine. Of these, tetrahydrofuran, chlorobenzene and methylnaphthalene are preferred. The above solvents may be used singly or in combination.

The X-type and/or  $\tau$ -type metal-free phthalocyanine is used at a ratio, to the binder resin, by weight of 1:1 to 1:10. If the phthalocyanine is used in amounts over the ratio of 1:1, the charging characteristic will be degraded, making it difficult to charge the resultant layer at a potential of not less than 500 volts, although the photosensitive characteristic is increased. On the contrary, when the binder is used in larger amounts than the ratio of 1:10, it will become difficult to impart a satisfactory photosensitive characteristic.

The dispersion or solution obtained above is coated onto a support or substrate such as a drum or a belt by means of bar coaters, calender coaters, spin coaters, blade coaters, dip coaters or gravure coaters in a dry thickness of 5 to 30 micrometers. The binder resin defined before is thermally curable. The coating layer is thermally cured at a temperature of from 100 to 200°C for 30 to 120 minutes to obtain a thermally cured film formed on the support. Since the binder resin is thermally cured, the film obtained is hard, dense and resistant to heat, thus leading to good printing resistance and good stability against ozone or unlikelihood for chemical fatigue. In addition, the binder resin used in the present invention is compatible with various types of photoconductors and solvents. Accordingly, if the binder resin is used in large amounts, a uniform film with good quality is obtained.

X-type and/or  $\tau$ -type metal-free phthalocyanine has been hereinabove described for application as a single layer structure wherein the phthalocyanine is treated in a specific way that it is partially dissolved in a molecular state and partially dispersed in a particulate state. The organic photosensitive material using the single-layer structure comprising the X-type and/or  $\tau$ -type metal-free phthalocyanine have the following advantages.

1. Since carrier transport agents which are relatively poor in heat resistance are not contained, the heat resistance is significantly better.
2. The sensitivity is very high and may arrives at 2 lux · second.
3. When X or  $\tau$ -type metal-free phthalocyanine is used, good sensitivity to light with a wide wavelength

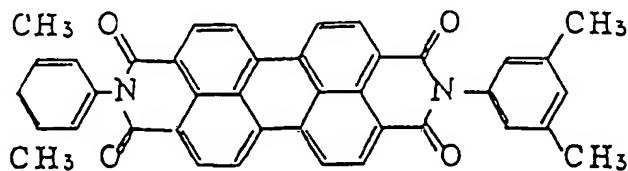
range of from 550 to 800 nm is ensured.

Although the embodiment using X-type and/or  $\tau$ -type metal-free phthalocyanine is preferred when the single-layer structure is used, other carrier generating agents may be used in combination with carrier transport agents by dispersion in a solvent of the type set out above along with the mixture of aromatic carboxylic acid and the binder resin. For this purpose, there are used metal-free phthalocyanine compounds such as  $\alpha$ ,  $\beta$ , X and  $\tau$ -type metal-free phthalocyanines, metal phthalocyanine compounds such as copper phthalocyanine, lead phthalocyanine, tin phthalocyanine, silicon phthalocyanine, vanadium phthalocyanine, chloroaluminium phthalocyanine, titanyl phthalocyanine, chloroindium phthalocyanine and chlorogallium phthalocyanine, and perylene compounds, thiapyrillium compounds, anthranthrone compounds, squalilium compounds, bisazo compounds, cyanine compounds, trisazo compounds, azulenium compounds and mixtures thereof. These compounds are specifically described in EP-A-408380. Specific examples of the compounds other than the metal and metal-free phthalocyanines include those of the following formulae.

1. Perylene compound of the following formula

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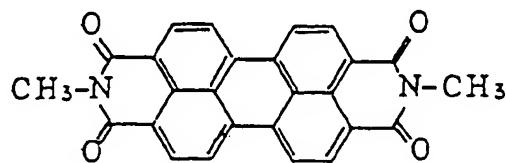
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2. Perylene compound of the following formula

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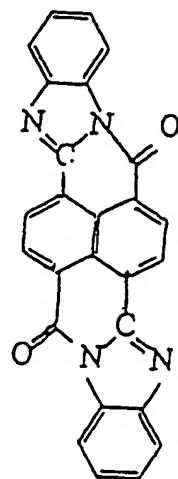
3. Compound of the following formula

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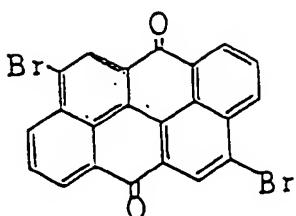
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4. Anthranthrone compound of the following formula

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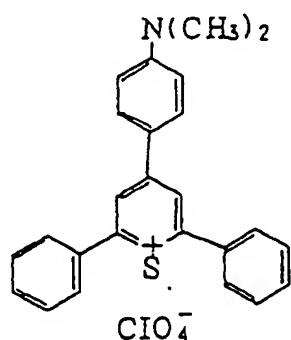
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5. Thiapyriliun compound of the following formula

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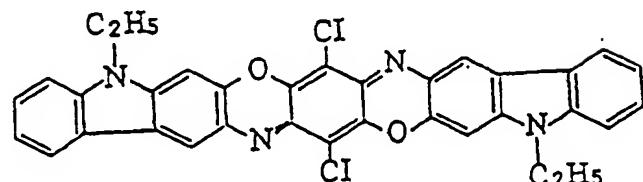
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6. Compound of the following formula

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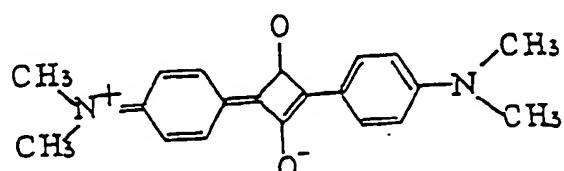
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7. Squalinium compound of the following formula

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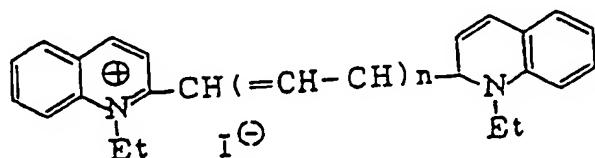
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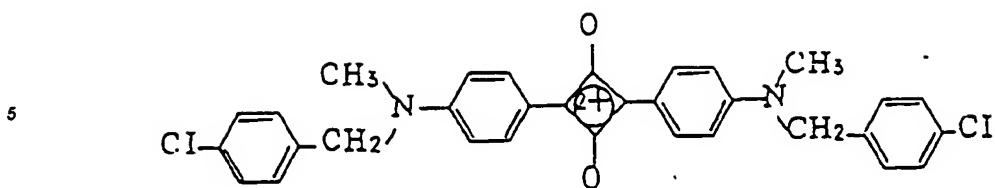
8. Cyanine compound of the following formula

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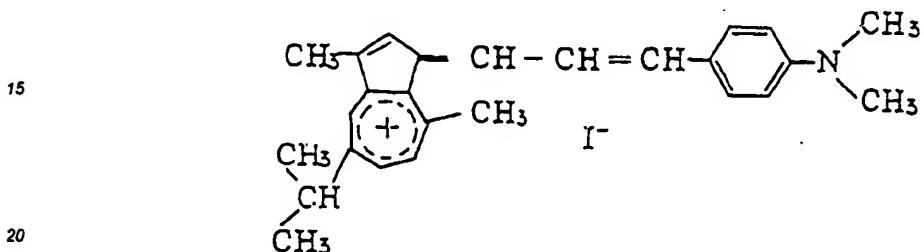
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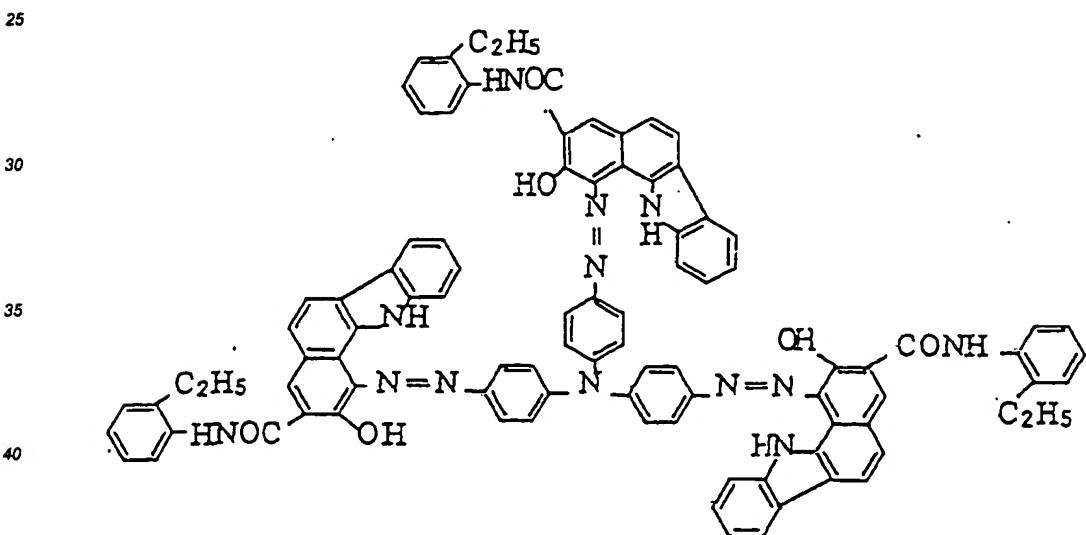
9. Squalinium compound of the following formula



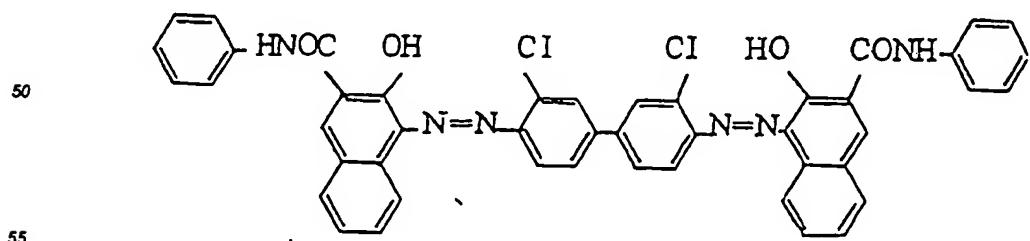
10 10. Azulenium dye of the following formula



11. Trisazo compound of the following formula



45 12. Diazo compound of the following formula



These carrier generation agents are preferably used in combination with carrier transport agents at a mixing ratio by weight of 1:1 to 1:0.01. Examples of the carrier transport agents may be any ones which are ordinarily used in the art and include, for example, hydrazone compounds, oxazole compounds, triphenylmethane

compounds and arylamine compounds. These may be used singly or in combination.

The organic photosensitive material using combinations of both agents in the single-layer structure has the following advantages.

- 5      (1) Such a material is suitable for use in a positive charge system.
- (2) The material is more stable and better in charging characteristic than known known single-layer structures.

(3) The durability and printing resistance are improved.  
 The incorporation of the aromatic carboxylic acid in the thermally cured binder polymer layer improves 10 the durability, the life and the heat resistance. Specific examples of the acid include 2-naphthoic acid, anthra-  
 cene-2-carboxylic acid, 1 or 2-naphthylacetic acid, 1 or 2-naphthoxyacetic acid, benzoic acid, benzylacetic acid,  
 bibenzoic acid, 2-biphenylcarboxylic acid, o-benzoylbenzoic acid and 4-benzoylbutyric acid. These acids may  
 be used singly or in combination.

15      The aromatic carboxylic acid is used in an amount of from 2 to 30 wt% based on the binder resin used. If the amount exceeds 30 wt%, the sensitivity is degraded.

The single-layer structure has been described as the photoconductive layer. The organic photosensitive material of the invention may further comprise a surface protective layer made of an insulating resin and formed on the thermally cured layer. Alternatively, a blocking layer may be provided between the support and the single-layer structure.

20      The double-layer structure formed on the support is then described.

This structure includes a carrier generation layer and a carrier transport layer. The carrier generation layer is formed by the use of a composition which comprises a mixture of aromatic carboxylic acid and a binder resin and a carrier generating agent as defined with respect to the single-layer structure. Alternatively, the carrier transport layer may be formed by the use of the mixture irrespective of whether the carrier transport layer is 25 formed on or below the carrier generation layer. If either of the layers is formed by the use of the mixture the other layer may make use of other binder resins including polyesters, polycarbonates, polymethacrylates, polystyrene, polyethers, various vinyl resins, various copolymers of the monomers used to prepare the above-indicated polymers, and blends thereof. Preferably, the mixture is used in both layers. The binder resin defined by the foregoing formula has very good miscibility with various carrier generating agents. Accordingly, if carrier 30 generating agents are used in large amounts, a uniform film with good quality is formed.

35      Among various carrier generating agents, X-type and/or  $\tau$ -type phthalocyanine is preferably used in the double-layer structure. More preferably, the phthalocyanine is mixed or kneaded in a solvent along with the mixture of aromatic carboxylic acid and binder resin to an extent sufficient to provide a two-phase dispersion where the phthalocyanine is partially dissolved in a molecular state and partially dispersed in a particulate state as set forth before. This is irrespective of the order of superposition of the two layers.

40      The carrier generation layer in the double-layer structure should preferably contain a carrier generating agent and a binder resin at a ratio by weight of 1:10 to 1:1.

Like the carrier generation layer, the carrier transport agent is generally used at a ratio, to the binder resin, by weight of 1:10 to 8:10.

45      It should be noted that if the carrier transport layer is formed on the carrier generation layer, the resultant double-layer structure is of the negatively charged type. This type of double-layer structure is, of course, within the scope of the invention. The drawbacks involved in known negative charge type photosensitive materials can be appropriately overcome by the use of the mixture of aromatic carboxylic acid and binder polymer defined in the present invention. In this case, the carrier generation layer is preferably formed using a polymer which is soluble in water or an alcohol and which is sparingly soluble in a solvent used for formation of the carrier transport layer although the mixture defined hereinbefore is also preferably used.

50      In the double-layer structure, an upper layer should preferably make use of the mixture of aromatic carboxylic acid and binder resin. The binder for the lower layer may be other resins as defined above but should preferably be the mixture defined before.

55      The carrier generation layer and the carrier transport layer should preferably have thicknesses of from 0.1 to 5 micrometers and from 10 to 50 micrometers, respectively.

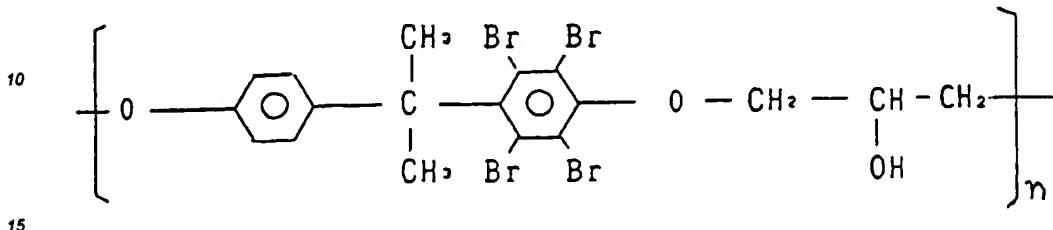
The respective layers may be formed similar to the case of the single-layer structure provided that the layer or layers containing the mixture defined before are thermally cured at a temperature of 100 to 200°C for 30 to 120 minutes.

55      The photosensitive material of the invention which has either a single-layer structure or a double-layer structure exhibit good sensitivity to light with a wide wavelength range of from 550 to 800 nm. Moreover, the photosensitive materials are applicable to various types of printing systems including duplicating machines, printers, facsimiles and the like.

The present invention is described in more detail by way of the following Examples.

EXAMPLE 1

5 X-type metal free-phthalocyanine (Fastogen Blue 8120B, made by Dainippon Inks Co., Ltd) and a binder polymer (FOC-10 available from Fuji Pharmaceutical Co., Ltd.) of the following formula:-



10 were dissolved in tetrahydrofuran at a ratio by weight of 1:4 and 5 wt% of 2-naphthoic acid, based on the binder polymer, are added followed by mixing by a ball milling technique. The resultant solution was applied onto an aluminium drum by dipping and thermally treated in air at 150°C for 2 hours to obtain a photosensitive material having a 25 μm thick single-layer structure.

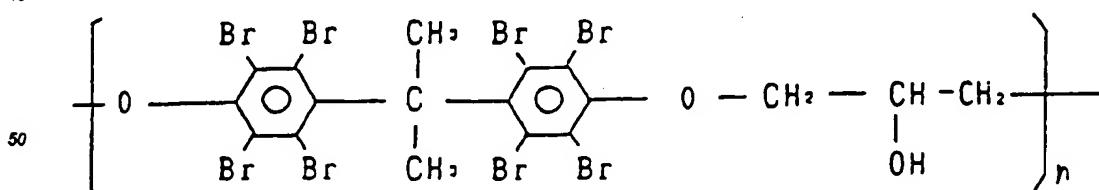
15 The thus obtained photosensitive material was subjected to measurement of photosensitive characteristics. More particularly, Paper Analyzer EPA-8100 was used to irradiate white light on a positively charged organic photosensitive material to measure a charge potential, a photosensitivity (half-life exposure,  $E_{1/2}$ ) and a residual potential,  $V_r$ . Similar measurements were made after subjecting the drum to a repetition test of 10,000 cycles. The results are shown in Table 1.

Table I

	Charge Potential lux · second	Photosensitivity Vr
immediately after fabrication	950 V	2.0 10 V
after 10,000 repetition cycles	890 V	1.8 8 V

## Example 2

40 X-type metal free-phthalocyanine (Fastogen Blue 8120B, made by Dainippon Inks Co., Ltd) and a binder polymer (FOC-12, available from Fuji Pharmaceutical Co., Ltd.) of the following formula:



45 were dissolved in cyclohexanone at a weight ratio of 1:5, 3 wt% of anthracene-2-carboxylic acid was added on the basis of the polymer, followed by mixing using a paint shaker. The resultant solution was applied onto an aluminium drum by dipping and thermally treated in air at 120°C for 4 hours to obtain a photosensitive material having a 20μm thick single-layer structure.

50 The thus obtained photosensitive material was subjected to measurement in the same manner as in Example 1 except that the number of repetition cycles were 20,000. The results are shown in Table 2 below.

TABLE 2

5	Charge Potential	Photosensitivity lux . second	Vr
10	immediately after fabrication	750 V	2.1
15	after 20,000 repetition cycles	750 V	1.9

The organic photosensitive materials obtained in Examples 1 and 2 were also subjected to measurement (including the repetition test) in an atmosphere of ozone wherein ozone generated from an ozone generator (Clean Load 300, available from Simon Co., Ltd.) was charged into the Paper Analyzer to make an ozone atmosphere. The ozone concentration was in the range of from 5 to 10 ppm. It was found that the results were similar to those obtained in the ozone-free condition.

Moreover, similar measurements were made under conditions of temperatures ranging from 5 to 40°C and relative humidities of from 20 to 85%. As a result, it was found that there was no significant difference.

Thus, the charge potential, photosensitivity, residual potential and ozone resistance are all excellent.

The general procedure of Example 2 was repeated, thereby forming organic photosensitive materials. The materials were mounted on a duplicator (Panasonic NP-1530) and a laser printer (Panasonic L-136) to evaluate the quality of images. In this test, the organic photosensitive materials were formed on several types of aluminium drums which were different from one another with respect to the surface roughness and the manner of washing of the drum surface. Any significant difference in the characteristics of the photosensitive materials was not found. From this, it will be seen that the quality of the final product for the photoconductors of the invention does not depend on the surface condition of the substrate. A good yield can be expected.

10,000 sheets of A4-size paper were printed with each of the duplicator and the laser printer, with the result that any image defect or blur was not found with a good printing resistance.

The organic photosensitive material obtained in Example 2 was subjected to a printing test wherein the thickness of the photosensitive layer was measured after repetition of 10,000 printing cycles. The thickness of 20 µm in each case was reduced to 19 µm after completion of the test. For comparison, the general procedure of Example 2 was repeated except that anthracene-2-carboxylic acid was not added. The resultant material was subjected to the printing test. The layer thickness of 20 µm was reduced to 15 µm but the image quality was substantially the same as that attained in Example 1. Thus, it will be seen that the aromatic carboxylic acid is effective in further improving the printing resistance and the ozone resistance.

### Example 3

A hydrazone compound (CTC-236, available from Anan Perfumes Co., Ltd) used as a carrier transport agent and FOC-10 with a bromination rate of 25% used as a binder polymer were dissolved in tetrahydrofuran at a ratio by weight of 2:3, to which 10 wt% of 2-naphthoic acid, based on the FOC-10 binder, followed by mixing by a ball milling. The resultant solution was applied onto an aluminium drum by dipping and thermally treated in air at 130°C for 2 hours to form a 18 µm thick carrier transport layer.

X-type metal-free phthalocyanine (Fastogen Blue 8120B) and a polyester used as a binder were dissolved in tetrahydrofuran at a ratio by weight of 1:1. The resulting solution was applied onto the carrier transport layer and thermally treated to form a 3 µm thick carrier generation layer, thereby obtaining a photosensitive drum.

The drum was subjected to measurement of a photosensitive characteristic, a charge potential and a residual potential, Vr, immediately after the fabrication and after repetition of 10,000 cycles. The photosensitive characteristics were determined by irradiating the positively charged drum with white light from a tungsten lamp by the use of Paper Analyzer EPA-8100.

The results are shown in Table 3 below.

Table 3

	Charge Potential	Photosensitivity lux · second	Vr
immediately after fabrication	850 V	1.8	35 V
after 10,000 repetition cycles	830 V	2.0	30 V

## Example 4

X-type metal-free phthalocyanine (Fastogen Blue 8120B) used as a carrier generation agent and FOC-12 with a bromination rate of 50% used as a binder were dissolved in tetrahydrofuran at a ratio by weight of 1:1, to which 3 wt% of anthracene-2-carboxylic acid, based on FOC-12, was further added, followed by mixing by ball milling. The resulting solution was applied onto an aluminium drum by dipping and thermally cured in air at 150°C for 2 hours to form a 1 μm thick carrier generation layer.

Separately, a hydrazone compound (CTC-236) used as a carrier transport agent and FOC-12 used above as a binder were dissolved along with 2-naphthoic acid in tetrahydrofuran at a ratio by weight of 1:5. The resultant solution was applied onto the carrier generation layer and thermally cured to form a 20 μm thick carrier transport layer, thereby obtain a photosensitive drum.

The drum was subjected to measurement of photosensitive characteristics by a negative charging procedure immediately after the fabrication and after a 20,000 repetition cycle test in the same manner as in Example 3. The results are shown in Table 4.

Table 4

	Charge Potential	Photosensitivity lux · second	Vr
immediately after fabrication	-950 V	2.2	-25 V
after 10,000 repetition cycles	-930 V	1.6	-20 V

The drum was further subjected to measurement of the photosensitive characteristics under conditions of a temperature of from 5 to 40°C and a relative humidity of from 20 to 85%. Similar results were obtained.

Moreover, fabrication of the drum was repeated several times and the drums were subjected to similar measurement. As a result, the drums could be fabricated reliably with uniform characteristics.

In addition, photosensitive drums were fabricated in the above procedure of Example 4 so that they could be set in a duplicator (Panasonic NP-1530) and a laser printer (Panasonic L-136), followed by evaluation of images.

In the above test, several types of drums were fabricated using aluminium drum substrates having different surface roughnesses and different manners of washing. As a result, it was found that there was little difference in the photosensitive characteristics depending on the surface roughness and the manner of washing.

In addition, 10,000 sheets of A4-size paper were printed with no defects being produced in the printed matters.

## Example 5

X-type metal free-phthalocyanine (Fastogen Blue 8120B, made by Dainippon Inks Co., Ltd.) and a binder

5 polymer of the formula indicated in Example 1 (FOC-10 with a bromination rate of 25%) were dissolved in tetrahydrofuran at a ratio by weight of 1:1, to which 5 wt% of 2-naphthoic acid, based on FOC-10, was added, followed by mixing by a ball milling technique. The resultant solution was applied onto an aluminium drum by dipping and thermally treated in air at 150°C for 2 hours to form a 1 μ m thick carrier generation layer.

A hydrazone compound used as a carrier transport agent (CTC-236) and a polyester used as a binder resin were dissolved in tetrahydrofuran at a ratio by weight of 4:10 and mixed under agitation. The resultant solution was applied onto the carrier generation layer and dried to form a 15 μ m thick carrier transport layer, thereby obtaining a double-layer structure formed on the aluminium drum.

10 The thus obtained photosensitive material was subjected to measurement of photosensitive characteristics in a negatively charged state in the same manner as in the foregoing examples immediately after the fabrication and after a 10,000 cycle repetition test. The results are shown in Table 5.

Table 5

	Charge Potential	Photosensitivity	Vr
	lux · second		
20 immediately after fabrication	-850 V	1.2	-20 V
25 after 10,000 repetition cycles	-830 V	1.1	-15 V

## Example 6

30 X-type metal-free phthalocyanine (Fastogen Blue 8120B) used as a carrier generation agent and FOC-12 with a bromination rate of 50% used as a binder were dissolved in cyclohexanone at a ratio by weight of 1:1, to which 3 wt% of anthracene-2-carboxylic acid, based on FOC-12, was further added, followed by mixing by ball milling. The resulting solution was applied onto an aluminium drum by dipping and thermally cured in air at 150°C for 2 hours to form a 1 μ m thick carrier generation layer.

35 Separately, a hydrazone compound (CTC-236) used as a carrier transport agent and FOC-12 used above as a binder were dissolved along with 2-naphthoic acid in cyclohexanone. The resultant solution was applied onto the carrier generation layer and thermally cured to form a 15 μ m thick carrier transport layer, thereby obtain a photosensitive drum.

The drum was subjected to measurement of photosensitive characteristics by a negative charging procedure immediately after the fabrication and after a 20,000 repetition cycle test in the same manner as in Example 40 5. The results are shown in Table 6.

Table 6

	Charge Potential	Photosensitivity	Vr
	lux · second		
45 immediately after fabrication	-950 V	1.2	-12 V
50 after 10,000 repetition cycles	-930 V	1.0	-15 V

55 The drum was further subjected to measurement of the photosensitive characteristics under conditions of a temperature of from 5 to 40°C and a relative humidity of from 20 to 85%. Similar results were obtained.

Moreover, fabrication of the drum was repeated several times and the drums were subjected to similar measurement. As a result, the drums could be fabricated reliably with uniform characteristics. From this, it will be found that the results of the repetition test by the negative charging procedure wherein ozone is inevitably

generated are so good that the ozone resistance is significantly improved.

In addition, photosensitive drums were fabricated in the above procedure of Example 4 so that they could be set in a duplicator (Panasonic NP-1530) and a laser printer (Panasonic L-136), followed by evaluation of images.

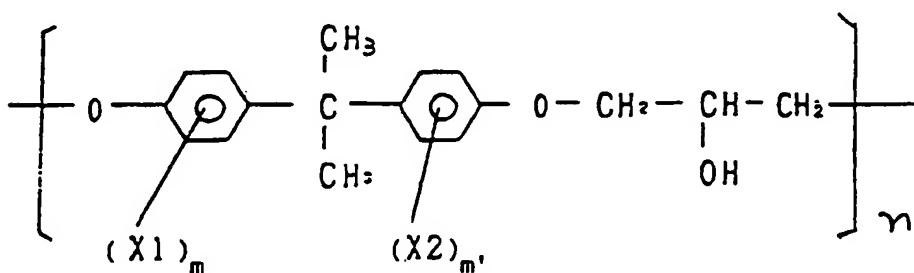
In the above test, several types of drums were fabricated using aluminium drum substrates having different surface roughnesses and different manners of washing. As a result, it was found that there was little difference in the photosensitive characteristics depending on the surface roughness and the manner of washing.

In addition, 10,000 sheets of A4-size paper were printed with no defects being produced in the printed matter.

When the general procedure of Example 5 was repeated except that 2-naphthoic acid was not added, the carrier generation layer was partially dissolved with tetrahydrofuran used for the formation of the carrier transport layer. As a result, a photosensitive material of good quality could not be obtained. To avoid this, the type of solvent for the carrier transport layer or the type of binder in the carrier generation layer has to be properly selected.

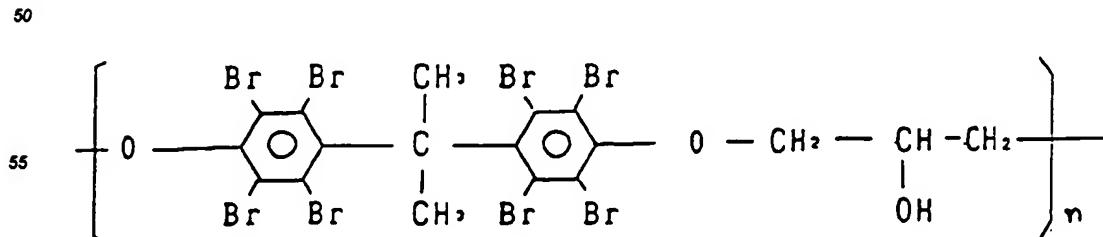
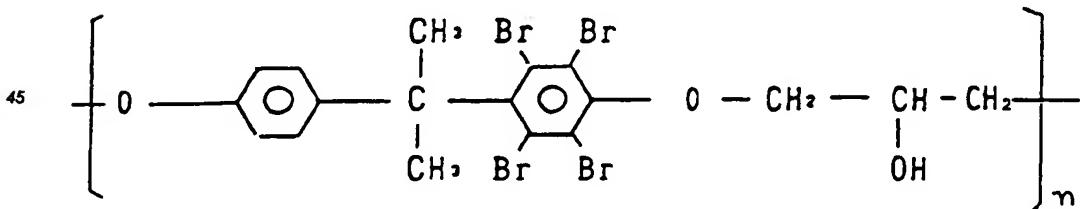
### Claims

1. A photosensitive material which comprises a conductive support and a layer structure formed on the support, said layer structure being made of a dispersion of an organic photoconductor in a mixture of an aromatic carboxylic acid comprising at least one benzene, naphthalene, anthracene or phenanthrene ring and a thermally cured binder polymer which has recurring units of the general formula:



wherein  $X_1$  and  $X_2$  represent a bromine atom,  $m$  and  $m'$ , which may be the same or different, are integers from 0 to 4, provided that  $m$  and  $m'$  are not both 0, and  $n$  is an integer of from 20 to 1000, the amount of aromatic carboxylic acid being from 2 to 30 wt% based on said binder polymer.

2. A photosensitive material according to claim 1, wherein said binder has recurring units of the formula



3. A photosensitive material according to claim 1 or 2, wherein said layer structure includes a single layer or two layers.
5. 4. A photosensitive material according to claim 3, wherein said single layer consists essentially of a cured film of a dispersion of X-type and/or  $\tau$ -type metal-free phthalocyanine in said mixture.
10. 5. A photosensitive material according to claim 4, wherein said X-type and/or  $\tau$ -type metal-free phthalocyanine is dispersed partially in a molecular state and partially in a particulate state.
15. 6. A photosensitive material according to claim 4, wherein said X-type and/or  $\tau$ -type metal-free phthalocyanine is used at a ratio by weight, to said binder polymer, of 1:10 to 1:1.
7. A photosensitive material according to claim 3, wherein said single layer comprises a dispersion of a carrier generation agent and a carrier transport agent in said mixture.
15. 8. A photosensitive material according to claim 3, wherein said double-layer structure includes a carrier generation layer and a carrier transport layer, one or both of which is made of a cured film of said mixture.
20. 9. A photosensitive material according to claim 8, wherein said carrier generation layer is formed on said carrier transport layer and is a cured film of a dispersion of a carrier generation agent in said mixture or said carrier transport layer is formed on said carrier generation layer and is a cured film of a dispersion of a carrier transport agent in said mixture.
25. 10. A photosensitive material according to claim 9, wherein said carrier generation agent is an X-type metal-free phthalocyanine and/or a  $\tau$ -type metal-free phthalocyanine.

#### Patentansprüche

30. 1. Lichtempfindliches Material, das einen leitfähigen Träger und eine auf dem Träger gebildete Schichtstruktur umfaßt, wobei diese Schicht hergestellt ist aus einer Dispersion eines organischen Fotoleiters in einer Mischung einer wenigstens einen Benzol-, Naphthalin-, Anthracen- oder Phenanthrenring umfassenden aromatischen Carbonsäure und eines thermisch ausgehärteten Bindemittelpolymeren, welches wiederkehrende Einheiten der allgemeinen Formel besitzt:

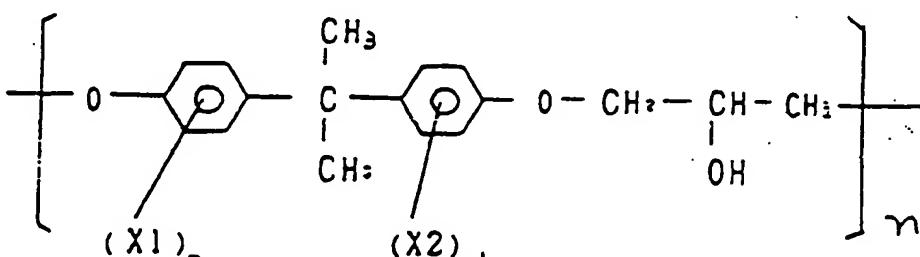
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1. Lichtempfindliches Material, das einen leitfähigen Träger und eine auf dem Träger gebildete Schichtstruktur umfaßt, wobei diese Schicht hergestellt ist aus einer Dispersion eines organischen Fotoleiters in einer Mischung einer wenigstens einen Benzol-, Naphthalin-, Anthracen- oder Phenanthrenring umfassenden aromatischen Carbonsäure und eines thermisch ausgehärteten Bindemittelpolymeren, welches wiederkehrende Einheiten der allgemeinen Formel besitzt:

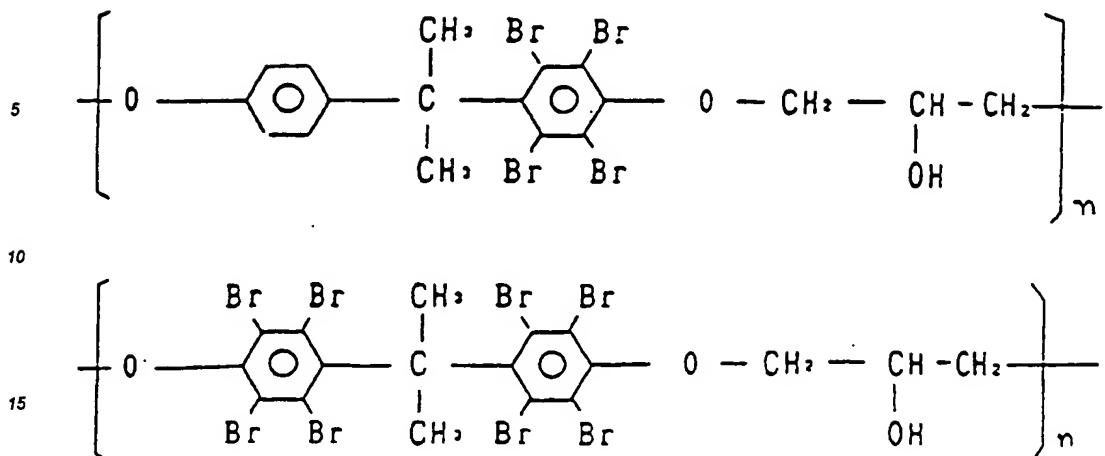


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worin  $X_1$  und  $X_2$  ein Bromatom darstellen,  $m$  und  $m'$ , die gleich oder verschieden sein können, ganze Zahlen von 0 bis 4 sind, vorausgesetzt daß  $m$  und  $m'$  nicht beide 0 sind, und  $n$  eine ganze Zahl von 20 bis 1000 ist, wobei die Menge an aromatischer Carbonsäure von 2 bis 30 Gew.-%, bezogen auf das Bindemittelpolymer, beträgt.

2. Lichtempfindliches Material nach Anspruch 1, worin dieses Bindemittel wiederkehrende Einheiten der Formel besitzt

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20 3. Lichtempfindliches Material nach Anspruch 1 oder 2, worin diese Schichtstruktur eine Einzelschicht oder zwei Schichten einschließt.

25 4. Lichtempfindliches Material nach Anspruch 3, worin diese Einzelschicht im wesentlichen aus einem ausgehärteten Film einer Dispersion von metallfreiem Phthalocyanin vom X-Typ und/oder  $\tau$ -Typ in dieser Mischung besteht.

30 5. Lichtempfindliches Material nach Anspruch 4, worin dieses metallfreie Phthalocyanin vom X-Typ und/oder  $\tau$ -Typ partiell in einem Molekülzustand und partiell in einem Teilchenzustand dispergiert ist.

35 6. Lichtempfindliches Material nach Anspruch 4, worin dieses metallfreie Phthalocyanin vom X-Typ und/oder  $\tau$ -Typ in einem Gewichtsverhältnis, bezogen auf das Bindemittelpolymeren, von 1:10 bis 1:1 verwendet wird.

7. Lichtempfindliches Material nach Anspruch 3, worin diese Einzelschicht eine Dispersion eines Trägererzeugungsmittels und eines Trägertransportmittels in dieser Mischung umfaßt.

35 8. Lichtempfindliches Material nach Anspruch 3, worin diese Doppelschichtstruktur eine Dispersion eines Trägererzeugungsmittels und eines Trägertransportmittels in dieser Mischung umfaßt, wobei eine oder beide aus einem ausgehärteten Film dieser Mischung hergestellt sind..

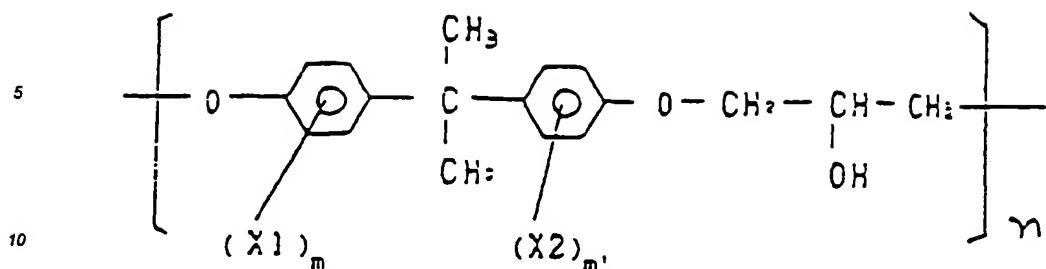
40 9. Lichtempfindliches Material nach Anspruch 8, worin diese Trägererzeugungsschicht auf dieser Trägertransportsschicht gebildet ist und ein ausgehärteter Film einer Dispersion eines Trägererzeugungsmittels in dieser Mischung ist oder diese Trägertransportsschicht auf dieser Trägererzeugungsschicht ausgebildet ist und ein ausgehärteter Film einer Dispersion eines Trägertransportmittels in dieser Mischung ist.

45 10. Lichtempfindliches Material nach Anspruch 9, worin dieses Trägererzeugungsmittel ein metallfreies Phthalocyanin vom X-Typ und/oder ein metallfreies Phthalocyanin vom  $\tau$ -Typ ist.

### **Revendications**

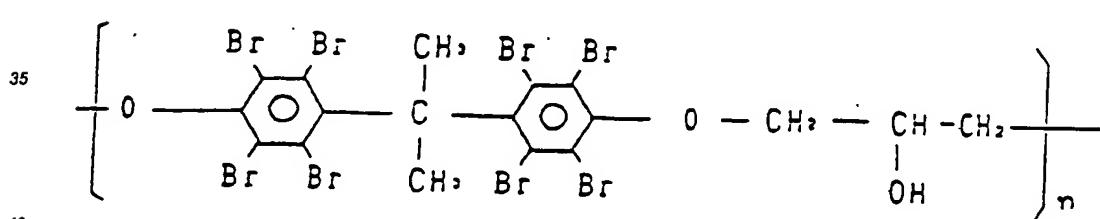
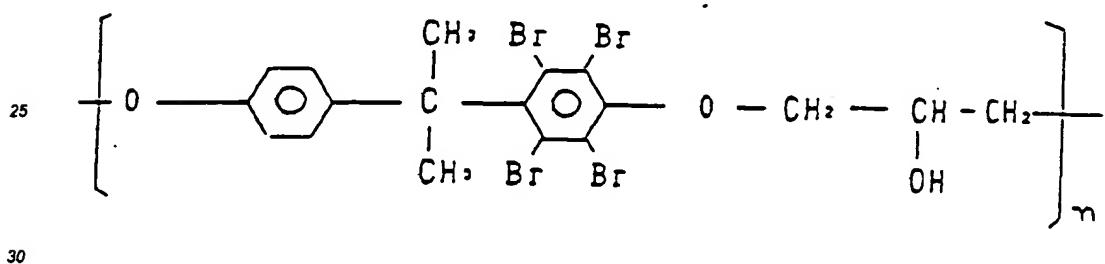
50 1. Matériau photosensible qui comprend un support conducteur et une structure de couche, formée sur le support, ladite structure de couche étant constituée d'une dispersion d'un photoconducteur organique dans un mélange d'un acide carboxylique aromatique, dont la molécule comporte au moins un noyau benzène, naphthalène, anthracène ou phénanthrène, et d'un liant à base d'un polymère thermodurcissable comportant des motifs répétés de formule générale :

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2. Matériau photosensible conforme à la revendication 1, dans lequel ledit liant comporte des motifs répétés de formule



3. Matériau photosensible conforme à la revendication 1 ou 2, dans lequel ladite structure de couche comporte une seule couche ou deux couches.

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4. Matériau photosensible conforme à la revendication 3, dans lequel ladite couche unique est constituée essentiellement d'une pellicule durcie d'une dispersion de phtalocyanine de type X et/ou de type τ, non-métallée, dans ledit mélange.

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5. Matériau photosensible conforme à la revendication 4, dans lequel ladite phtalocyanine de type X et/ou de type τ, non-métallée, est dispersée en partie à l'état de molécules et en partie à l'état de particules.

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6. Matériau photosensible conforme à la revendication 4, dans lequel ladite phtalocyanine de type X et/ou de type τ, non-métallée, est utilisée en une proportion pondérale, par rapport audit liant polymère, valant de 1/10 à 1/1.

7. Matériau photosensible conforme à la revendication 3, dans lequel ladite couche unique comprend une dispersion d'un agent de génération de porteurs et d'un agent de transport de porteurs dans ledit mélange.

8. Matériau photosensible conforme à la revendication 3, dans lequel ladite structure à deux couches comporte une couche de génération de porteurs et une couche de transport de porteurs, dont l'une ou

les deux sont faites d'une pellicule durcie dudit mélange.

5        9. Matériau photosensible conforme à la revendication 8, dans lequel ladite couche de génération de porteurs est formée par-dessus ladite couche de transport de porteurs et est constituée d'une pellicule durcie d'une dispersion d'un agent de génération de porteurs dans ledit mélange, ou bien ladite couche de transport de porteurs est formée par-dessus ladite couche de génération de porteurs et est constituée d'une pellicule durcie d'une dispersion de l'agent de transport de porteurs dans ledit mélange.

10      10. Matériau photosensible conforme à la revendication 9, dans lequel ledit agent de génération de porteurs est une phtalocyanine de type X non-métallée et/ou une phtalocyanine de type τ non-métallée.

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